United States Environmental Protection Agency					Work Assignment Number				
EPA		Washington, DC 20460				1-06			
LFA	Work A	ssignment			Other	Amendm	nent Number:		
Contract Number Contract Period 04/29/2011 To 03/28/2012					Title of Work Assignment/SF Site Name				
EP-D-11-006	P-D-11-006 Base X Option Period Number				Cerium Ambient Sampling				
Contractor	INC		Section and par	ragraph of Cont	ract SOW				
EASTERN RESEARCH GROUP  Purpose:   V Made Assistance	, INC.	G T 1862-18 A 22 A	N O. I		Period of Performance	20			
Work Assignment	Work Assignment Close-Out				renou or renormance				
Work Assignment Amendment Incremental Funding					From 08/19/2011 To 03/28/2012				
Work Plan Approva	al				1.0 007 137	2011 10 00	72072012		
This work assignment include									
assignment. To the best of beign performed by this offi		ork does not du	iplicate an	ıy work pr	eviously perfor	med or curre	ntly		
Superfund	Acc	ounting and Approp	oriations Data	Ĩ		Χ	Non-Superfund		
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(Max 2)									
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04/29/2011 To 03/28/2012									
This Action:					<b>3</b> 50				
Total: 350									
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(Signature) (Date)				FAX	FAX Number:				
Contracting Official Name Rodney-Daryl Jones				Bran	Branch/Mail Code:				
				Phor	e Number: 919-	-541-3112			
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#### STATEMENT OF WORK

I. Title: AMAD Ambient Cerium Particulate Sampling Work

**Contractor Name:** ERG Inc. EP-D-11-006

**WA #:** 1-06

# II. Work Assignment Manager (WAM)

WAM Name: William Benjey

U.S. Environmental Protection Agency

Program Office: ORD

Division/Lab: AMAD/NERL Mail Code: E-243-01

City, State, Zip Code: Research Triangle Park, NC 27711

Phone w/area code: 919-541-0821

## III. Background:

Diesel vehicles are a major source of particulate matter. In an attempt to reduce PM2.5 emissions and increase fuel efficiency, nanoparticle fuel additives have been developed, several of which are based on cerium oxide. The Envirox<sup>TM</sup> diesel additive has been regularly used outside the U.S., including in a Stagecoach bus fleet in Newcastle, United Kingdom. The Newcastle Center Automatic Urban and Rural Monitoring Network location, near a major Newcastle bus depot, revealed increased cerium oxide levels in PM10 following widespread adoption of the nano cerium fuel additive in 2005 [Park et al., 2008]. For this work, size-segregated sampling of ambient PM will be conducted at the Newcastle Civic Center at Newcastle-upon-Tyne on St. Mary's Place in the United Kingdom [DEFRA, 2011]. Alternate locations may be considered if significant use of nanoCerium fuel additives near the site can be demonstrated to lead to detectable cerium levels in ambient particulate matter. The COR must approve any changes in site location, following written justification of a site change. Note that London, Marylebone did not show a statistically significant increase in ambient cerium concentrations following implementation of the catalyst [Park et al., 2008]. Park et al. [2008] predict loadings on the order of 40 ng Cerium/mg PM10 at the Newcastle site and data obtained from Ian Mudway by Garnet Erdakos indicates November/December ambient loadings were approximately 60-70 ng cerium/mg PM10 in 2005.

# IV. Description and Tasks:

The purpose of this work is to characterize near-road concentrations and deposition influenced by emissions from diesel vehicles using cerium oxide based fuel borne catalysts. This shall include size-segregated sampling of ambient particulate matter in addition to the collection of plant samples. Deliverables from the work include reports, plant samples, filter samples, and sample analysis. The work shall be completed in two phases with the goal of the first phase to provide information for a more complete second phase.

Phase I is limited in scope and provides the foundation for the full-scale effort in Phase II. The objective of Phase I is to collect and identify cerium in ambient samples. The EPA will conduct all analysis of the filter samples during phase I. The deliverables for this phase are exposed

filters, blanks, and field notes documenting the sampling and any important events. Phase I shall also gather information to prepare for plant sampling. Phase II shall not proceed without written technical direction from the COR that phase I is complete.

Phase II will consist of a longer sampling period, include collection of plant samples, and attribution of the ambient cerium to diesel exhaust. Information from phase I will determine the appropriate duration of sampling. For Phase II, a sampler with multiple size segregations below 100nm is most desired, but Phase I will be able to guide whether or not a coarse size-segregation will be adequate. A minimum of three samples for ICP-MS bulk analysis (in-house EPA) will be collected along with several samples for Transmission Electron Microscopy (TEM) analysis (to be performed as part of this work order). The plant(s) identified in phase I will be collected and mailed to the EPA in Corvallis, Oregon for analysis. Two sets of PM10 samples, at high and low traffic times respectively, shall also be collected to attribute ambient cerium levels to diesel exhaust.

The contractor shall perform the following tasks:

# I. PHASE I [To be completed by February 29, 2012]

- a. Develop an initial project work plan for this work assignment. Report should be delivered as an electronic file in Word Document file format. [Due within three weeks of receipt of the work assignment from EPA]. The workplan shall contain:
  - i. Verification of use of the Envirox additive by Stagecoach buses in Newcastle and any potential suspension/changes in schedule of use of the additive.
  - ii. The bus schedules for buses near the site using and not using the additive.
  - iii. A reasonable assessment of possible cerium sources other than the fuel additive, such as wintertime road treatments, that may release cerium into the ambient air.
  - iv. Access to the Newcastle AURN sampling site and any modifications needed. Recent photographs and a detailed description of the sampling site location and surrounding vegetation and buildings should be provided.
  - v. Identification of possible plant species (2-3) near the ambient sampling site (Latin binomial scientific name) to be sampled during Phase II. This information will be used by the EPA to obtain permits for receiving the samples in the U.S. and preparing a sampling and handling protocol. The contractor is responsible for obtaining any permits or adhering to any protocols required by the UK.
- b. Prepare a Quality Assurance Project Plan (QAPP) for phase I of the work assignment. The QAPP shall be prepared in accordance with EPA guidance (EPA-AQ\_R-5), and include a description of QA/QC steps to be followed for each task of this work assignment and persons responsible. The contractor shall revise the QAPP based on EPA comments and provide a final version. A summary QA report in electronic form (Word) shall be delivered, describing test results from each task of the work assignment. [Due November 15, 2011]

c. Conduct three size-segregated sampling events, each 2 days in duration, over the course of 3 weeks. Samples shall be collected on the same days the week with the Teflon filters in a size-selecting type instrument. One 24-hour sampling event, with TEM grids, should also occur using at the Newcastle site. [Due February 29, 2012]

All exposed and blank filters should be sent to the US EPA in Research Triangle Park, North Carolina, USA for analysis.

- II. PHASE II [ To be completed by March 31, 2012] Tasks are subject to revision following the outcome of Phase I. Written permission from the EPA must be obtained before Phase II can proceed. The contractor shall
  - a. Develop a project work plan for the second phase of this work assignment. Report should be delivered as an electronic file in Word Document format for 8.5 by 11 inch paper. [Due March 31, 2012].
  - b. Prepare a revised Quality Assurance Project Plan (QAPP) for phase II of the work assignment. The QAPP shall be prepared in accordance with EPA guidance (EPA-AQ\_R-5), EPA Requirements for Quality Assurance Project Plans for Environmental Data Operations," which is available from the Internet at "www.epa.gov/quality/qapps.html, contain all of the elements included in a site-specific test plan for emissions testing programs, as described in the guidebook, "Preparation and Review of Site-Specific Test Plans," incorporated herein by reference, which is available on the EPA's Emission Measurement Center website at <a href="www.epa.gov/ttn/emc">www.epa.gov/ttn/emc</a>, and include a description of QA/QC steps to be followed for each task of this work assignment and persons responsible. The contractor shall revise the QAPP based on EPA comments and provide a final version. A summary QA report in electronic form shall be delivered, describing test results from each task of the work assignment. [Due January 31, 2012]
  - c. Provide an SOP for the TEM analysis. EPA will review and approve the SOP. [Due February 29, , 2012]
  - d. Obtain size segregated samples of ambient particulate matter. Sampling should take place over the course of at least 2 weeks but may be longer or shorter based on the Phase I results. [Due March 31, 2012] The following is required:
    - i. Exposed Teflon filters and blanks shall be sent to the EPA in Research Triangle Park, NC, USA for ICP-MS analysis. The contractor shall be responsible for Transmission Electron Microscopy (TEM) or similar analysis to classify cerium particle size and mixing state. The existence of any of the following should be noted and images included in draft and final reports, including:
      - 1. Cerium oxide particles in primary form unattached to soot (approximately 5-10 nm in diameter)
      - 2. Cerium oxide agglomerates, aggregates, or formations larger than primary size.
      - 3. Cerium oxide attached to soot.
      - 4. Cerium oxide inclusions in other materials
      - 5. Other cerium oxide or soot particles that are not mixed.

- e. In addition to the size-segregated sampling, PM10 samples shall be collected at the same time as the other samples with one set devoted to high bus-traffic times and the other set devoted to low bus traffic times. Filters shall be sent to the EPA for bulk analysis. [Due March 31, 2012]
- f. Collect vegetation samples to be shipped to the EPA in Corvallis, Oregon, USA. EPA will provide information on shipping and handling procedures based on the outcome of Phase I. [Due March 31, 2012]
- g. Collect continuous meteorological data including temperature, pressure, relative humidity, windspeed, wind direction, height of windspeed measurement, and mixing height.
- h. Continuously collect high resolution video during sample collection to capture the bus identification numbers and visible exhaust during sampling periods.
- i. Collect microaethalometer measurements of black carbon continuously during sampling periods.
- j. Provide a draft final report in EPA report format, using Word. The reports shall describe the sampling rationale, protocol, sampling completed, analysis performed by the contractor and a descriptive, graphical and statistical summary of monitoring results.[Due September 1, 2012]
- k. Provide a final report in EPA report format, reflecting EPA comments on the draft report. [Due March 31, 2012]

## REFERENCES

Department for Environment Food and Rural Affairs (DEFRA) (2011), AURN Site Information: Newcastle Center, http://uk-air.defra.gov.uk/networks/aurn-site-info?site\_id=NEWC and http://aurn.defra.gov.uk/stations/viewStation.php?id=82.

Park, B., K. Donaldson, R. Duffin, L. Tran, F. Kelly, I. Mudway, J.-P. Morin, R. Guest, P. Jenkinson, Z. Samaras, M. Giannouli, H. Kouridis, and P. Martin (2008), Hazard and risk assessment of a nanoparticulate cerium oxide-based diesel fuel additive—a case study, *Inhalation Toxicology*, 20(6), 547-566.

	United States Environm	United States Environmental Protection Agency			Work Assignment Number				
EDA		Washington, DC 20460				1-06			
EPA	Work As	ssignment				Other	X Amenda	nent Number:	
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Contractor			Section and pa	ragraph of Con	tract SOW		*		
EASTERN RESEARCH GROUP	, INC.								
Purpose: Work Assignment		Work Assignment C	Close-Out		Period of Performance				
X Work Assignment Amendment Incremental Funding									
Work Plan Approva	al				From 08/19/2011 To 03/28/2012				
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## AMAD Ambient Cerium Particulate Sampling Work

I. Title: Cerium Ambient Sampling

Contractor Name: ERG Inc.
Contract #: EP-D-11-006
Work Assignment: 1-06 change 1

## II. Background:

Diesel vehicles are a major source of particulate matter. In an attempt to reduce PM2.5 emissions and increase fuel efficiency, nanoparticle fuel additives have been developed, several of which are based on cerium oxide. The Envirox<sup>TM</sup> diesel additive has been regularly used outside the U.S., including in a Stagecoach bus fleet in Newcastle, United Kingdom. The Newcastle Center Automatic Urban and Rural Monitoring Network location, near a major Newcastle bus depot, revealed increased cerium oxide levels in PM10 following widespread adoption of the nano cerium fuel additive in 2005 [Park et al., 2008]. For this work, size-segregated sampling of ambient PM will be conducted at the Newcastle Civic Center at Newcastle-upon-Tyne on St. Mary's Place in the United Kingdom [DEFRA, 2011]. Alternate locations may be considered if significant use of nanoCerium fuel additives near the site can be demonstrated to lead to detectable cerium levels in ambient particulate matter. The COR must approve any changes in site location, following written justification of a site change. Note that London, Marylebone did not show a statistically significant increase in ambient cerium concentrations following implementation of the catalyst [Park et al., 2008]. Park et al. [2008] predict loadings on the order of 40 ng Cerium/mg PM10 at the Newcastle site and data obtained from Ian Mudway by Garnet Erdakos indicates November/December ambient loadings were approximately 60-70 ng cerium/mg PM10 in 2005.

# III. Description and Tasks:

The purpose of this work is to characterize near-road concentrations and deposition influenced by emissions from diesel vehicles using cerium oxide based fuel borne catalysts. This shall include size-segregated sampling of ambient particulate matter in addition to the collection of plant samples. Deliverables from the work include reports, plant samples, filter samples, and sample analysis. The work shall be completed in two phases with the goal of the first phase to provide information for a more complete second phase.

Phase I is limited in scope and provides the foundation for the full-scale effort in Phase II. The objective of Phase I is to collect and identify cerium in ambient samples. The EPA will conduct all analysis of the filter samples during phase I. The results of the analysis will be provided to the contractor for use in their planning and reporting. In phase I, the EPA may provide the Microorifice uniform deposition impactors (MOUDI) sampler, three complete sets of pre-weighed and mounted filters, and ancillary meteorological equipment. The contractor shall be responsible for shipment and any customs clearances of equipment. A list of the equipment that may be provided is listed in Appendix A. Teflon-based filters for use in the MOUDI (3x12=36 filters), 3 backup filters, 4 blanks, and one set of quartz based filters (unmounted). If the equipment is provided by EPA, the contractor assumes responsibility for operating the MOUDI and repairing or replacing the instrument in the event of any damage or theft. The terms and conditions of loan are specified in Appendix B. The deliverables for this phase are the exposed filters, returned blanks, and field notes documenting the sampling and any important events. Phase I is also to gather information to prepare for plant sampling. Phase II shall not proceed without written prior approval from the COR that phase I is complete.

Phase II will consist of a longer sampling period, include collection of plant samples, and attribution of the ambient cerium to diesel exhaust. Information from phase I will determine the appropriate duration of sampling. For Phase II, a sampler with more size segregations below 100nm than a MOUDI is most desired (such as, but not limited to, a nano-MOUDI), but Phase I will be able to guide whether or not a coarse size-segregation will be adequate. A minimum of three samples for ICP-MS bulk analysis (in-house EPA) will be collected along with several samples for Transmission Electron Microscopy (TEM) analysis (to be performed as part of this work order). The plant(s) identified in phase I will be collected and mailed to the EPA in Corvallis, Oregon for analysis. A dual-channel PM10 sampler, to sample at high and low traffic times, should also be deployed to attribute ambient cerium levels to diesel exhaust.

The contractor shall perform the following tasks:

## I. PHASE I [To be completed by February 29, 2012]

- a. Develop an initial project work plan for this work assignment. Report should be delivered as an electronic file in Word Document file format. [Due within three weeks of receipt of the work assignment from EPA]. The work plan shall contain:
  - i. Verification of use of the Envirox additive by Stagecoach buses in Newcastle and any potential suspension/changes in schedule of use of the additive.
  - ii. The bus schedules for buses near the site using and not using the additive.
  - iii. A reasonable assessment of possible cerium sources other than the fuel additive, such as wintertime road treatments, that may release cerium into the ambient air.
  - iv. Access to the Newcastle AURN sampling site and any modifications needed. Recent photographs and a detailed description of the sampling site location and surrounding vegetation and buildings should be provided.
  - v. Identification of possible plant species (2-3) near the ambient sampling site (Latin binomial scientific name) to be sampled during Phase II. This information will be used by the EPA to obtain permits for receiving the samples in the U.S. and preparing a sampling and handling protocol. The contractor is responsible for obtaining any permits or adhering to any protocols required by the UK.
- b. Prepare a Quality Assurance Project Plan (QAPP) for phase I of the work assignment. The QAPP shall be prepared in accordance with EPA guidance (EPA-AQ\_R-5), and include a description of QA/QC steps to be followed for each task of this work assignment and persons responsible. The contractor shall revise the QAPP based on EPA comments and provide a final version. A summary QA report in electronic form (Word) shall be delivered, describing test results from each task of the work assignment. [Due November 15, 2011]
- c. Conduct three size-segregated sampling events, each 2 days in duration, over the course of 3 weeks. Samples shall be collected on the same days the week with the Teflon filters in a size-selecting type instrument. One 24-hour sampling event,

with TEM grids, should also occur using at the Newcastle site. [Due February 29, 2012]

- i. The MOUDI sampler may be provided to ERG as Government Furnished Equipment (GFE) via pickup by the contractor at the EPA in Research Triangle Park, North Carolina, USA. The contractor shall be responsible for shipping, field installation, monitoring, and the safe return of the sampler.
- **ii.** All exposed and blank filters shall be returned to the US EPA in Research Triangle Park, North Carolina, USA for analysis.
- II. PHASE II [ Parts not addressed may be addressed in a future work assignment] Tasks are subject to revision following the outcome of Phase I. Written permission through Technical Direction (TD) from the EPA must be obtained before Phase II can proceed. The contractor shall
  - a. Develop a project work plan for the second phase of this work assignment.
     Report should be delivered as an electronic file in Word Document format for 8.5 by 11 inch paper. [Due March 28, 2012].
  - b. Prepare a revised Quality Assurance Project Plan (QAPP) for phase II of the work assignment. The QAPP shall be prepared in accordance with EPA guidance (EPA-AQ\_R-5), EPA Requirements for Quality Assurance Project Plans for Environmental Data Operations," which is available from the Internet at "www.epa.gov/quality/qapps.html, contain all of the elements included in a site-specific test plan for emissions testing programs, as described in the guidebook, "Preparation and Review of Site-Specific Test Plans," incorporated herein by reference, which is available on the EPA's Emission Measurement Center website at <a href="www.epa.gov/ttn/emc">www.epa.gov/ttn/emc</a>, and include a description of QA/QC steps to be followed for each task of this work assignment and persons responsible. The contractor shall revise the QAPP based on EPA comments and provide a final version. A summary QA report in electronic form shall be delivered, describing test results from each task of the work assignment. [Due January 31, 2012]
  - c. Provide an SOP for the TEM analysis. EPA will review and approve the SOP. [Due February 29, , 2012]

NOTE: Additional sampling, including particulate matter, site video and meteorological observations in Phase II may be specified in a follow-on work assignment.

### REFERENCES

Department for Environment Food and Rural Affairs (DEFRA) (2011), AURN Site Information: Newcastle Center, http://uk-air.defra.gov.uk/networks/aurn-site-info?site\_id=NEWC and http://aurn.defra.gov.uk/stations/viewStation.php?id=82.

Park, B., K. Donaldson, R. Duffin, L. Tran, F. Kelly, I. Mudway, J.-P. Morin, R. Guest, P. Jenkinson, Z. Samaras, M. Giannouli, H. Kouridis, and P. Martin (2008), Hazard and risk assessment of a nanoparticulate cerium oxide-based diesel fuel additive—a case study, *Inhalation Toxicology*, 20(6), 547-566.

### APPENDIX A

Government Furnished Property (GFP) that may be provided by EPA

Item	Description	Serial #	EPA Decal	Comments
	Ten-Stage Non-Rotating Micro-Orifice Uniform			
1	Deposit Impactor (MOUDI), Model 116-NR, with	MDI-110-NR-362	B13069	
	pumping unit.			
2	Dual Channel PM10 Sampler	2-01D-A100	N/A	
2	Computerized Sampling Dump (for item 2).	3-02QAD-B0327	N/A	Property of Florida Dept. of Environmental Protection, Decal #135294
*	Model URG-3000-02QAD	3-02QAD-00327	,,,,	-roperty of Horida Dept. of Environmental -rotection, Decar #155254
4	microaethelometer 1	TBD	TBD	
6	microaethelometer 2	TBD	TBD	
6	sonic met station 1	TBD	TBD	
7	sonic met station 2	TBD	TBD	

Critical characteristics of the EPA-owned MOUDI sample include: (1) an adequate flow rate (the EPA MOUDI flow rate is 30 lpm); (2) ability to collect size-resolved samples on both 47 mm teflon filters and TEM grids; and (3) sufficient size-resolution to meet your modeling needs (the EPA MOUDI has the following stage cutpoints: 0.056, 0.10, 0.18, 0.32, 0.56, 1.0, 1.8, 3.2, 5.6, 10, and 18 µm).

### APPENDIX B

Terms and conditions of GFP loan

- 1. The Recipient shall:
  - a. return the loaned property in like condition as when received from EPA, normal wear and tear excepted, and free of contamination, on or before the expiration date (as set forth in Section 2 of the first page of this Loan Agreement), unless the loan period is formally extended or terminated before the expiration date;
  - b. in case ofloss or damage of the loaned property, reimburse EPA at the current price of the replacement or repair;
  - c. assume all cost involved in preparing, handling, loading, disconnecting, and transporting the loaned property from and to EPA;
  - d. indemnify and hold harmless the United States against any and all liability loss, damages, claims, and costs incidental thereto as a result of Recipient's use or possession of the loaned property; and
  - e. use the loaned property only for the purpose specified in the loan agreement.
- 2. The loaned property shall not be modified, loaned, or transferred to a third party without the prior written permission of EPA.
- 3. The Recipient shall account for, or permit physical inspection of, the loaned property by EPA after notification from EPA.
- 4. Title to the loaned property is vested in and will remain with the United States and the loaned property shall be used only for official purposes.